

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|--|
| (51) International Patent Classification ⁶ : C01B 3/36 | A1 | (11) International Publication Number: WO 96/39354 (43) International Publication Date: 12 December 1996 (12.12.96) |
| (21) International Application Number: PCT/EP96/02469 (22) International Filing Date: 5 June 1996 (05.06.96) (30) Priority Data: 95201487.6 6 June 1995 (06.06.95) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors: OORTWIJN, Peter; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). WENTINCK, Hendrik, Martinus; Badhuisweg 3, NL-1031 CM Amsterdam (NL). | | (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: A METHOD FOR FLAME STABILIZATION IN A PROCESS FOR PREPARING SYNTHESIS GAS (57) Abstract <p>A method for stabilizing the flame on the tips of burner internals in a process for preparing synthesis gas by partial oxidation of a gaseous hydrocarbon-containing fuel comprising the steps of: a) supplying a gaseous hydrocarbon-containing fuel, a moderator gas and an oxidiser through a burner to a reactor, wherein the mass flow of the moderator gas is adjusted such that the moderator gas concentration does not exceed a predetermined limit; b) effecting process conditions such that the flame is contacting the burner internal tips; c) re-adjusting the velocities and mass flows of the fuel and/or oxidiser and/or moderator gas in case of flame-lifting from the burner internal tips in such a manner that the flame is restabilized on the burner internal tips; and wherein in step c) the moderator gas concentration does not exceed the said limit of step a).</p> | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|--|----|--------------------------|
| AM | Armenia | GB | United Kingdom | MW | Malawi |
| AT | Austria | GE | Georgia | MX | Mexico |
| AU | Australia | GN | Guinea | NE | Niger |
| BB | Barbados | GR | Greece | NL | Netherlands |
| BE | Belgium | HU | Hungary | NO | Norway |
| BF | Burkina Faso | IE | Ireland | NZ | New Zealand |
| BG | Bulgaria | IT | Italy | PL | Poland |
| BJ | Benin | JP | Japan | PT | Portugal |
| BR | Brazil | KE | Kenya | RO | Romania |
| BY | Belarus | KG | Kyrgyzstan | RU | Russian Federation |
| CA | Canada | KP | Democratic People's Republic of Korea | SD | Sudan |
| CF | Central African Republic | KR | Republic of Korea | SE | Sweden |
| CG | Congo | KZ | Kazakhstan | SG | Singapore |
| CH | Switzerland | LJ | Liechtenstein | SI | Slovenia |
| CI | Côte d'Ivoire | LK | Sri Lanka | SK | Slovakia |
| CM | Cameroon | LR | Liberia | SN | Senegal |
| CN | China | LT | Lithuania | SZ | Swaziland |
| CS | Czechoslovakia | LU | Luxembourg | TD | Chad |
| CZ | Czech Republic | LV | Latvia | TG | Togo |
| DE | Germany | MC | Monaco | TJ | Tajikistan |
| DK | Denmark | MD | Republic of Moldova | TT | Trinidad and Tobago |
| EE | Estonia | MG | Madagascar | UA | Ukraine |
| ES | Spain | ML | Mali | UG | Uganda |
| FI | Finland | MN | Mongolia | US | United States of America |
| FR | France | MR | Mauritania | UZ | Uzbekistan |
| GA | Gabon | | | VN | Viet Nam |

A METHOD FOR FLAME STABILIZATION IN A PROCESS FOR
PREPARING SYNTHESIS GAS

The present invention relates to a method for flame stabilization in a process for preparing synthesis gas by partial oxidation of a gaseous hydrocarbon-containing fuel and an oxygen-containing gas.

5 In such a process for preparing synthesis gas an oxygen-containing gas, which is applied as an oxidiser, and a gaseous hydrocarbon-containing fuel are supplied to a gasification zone through a burner, e.g. a multi-orifice (co-annular) burner comprising a concentric
10 arrangement of n passages or channels coaxial with the longitudinal axis of said burner, wherein n is an integer > 2 , and wherein autothermically a gaseous stream containing synthesis gas is produced under appropriate conditions.

15 Such co-annular burners contain substantially cylindrical internals which separate the oxidiser and the hydrocarbon-containing fuel until they reach the burner exit.

The oxygen-containing gas, which is applied as an
20 oxidiser, is usually air or (pure) oxygen or steam or a mixture thereof. In order to control the temperature in the gasification zone a moderator gas (for example steam, water or carbon dioxide or a combination thereof) can be supplied to said zone. The moderator gas can be
25 supplied through the fuel channel, the oxidiser channel or a separate channel of the burner.

Those skilled in the art will know the conditions of applying oxidiser and moderator gas.

Synthesis gas is a gas comprising carbon monoxide
30 and hydrogen, and it is used, for example, as a clean

- 2 -

medium-calorific value fuel gas or as a feedstock for the synthesis of methanol, ammonia or hydrocarbons, which latter synthesis yields gaseous hydrocarbons and liquid hydrocarbons such as gasoline, middle
5 distillates, lub oils and waxes.

In the specification and in the claims the term gaseous hydrocarbon-containing fuel will be used to refer to hydrocarbon-containing fuel that is gaseous at gasifier feed pressure and temperature.

10 According to an established process, synthesis gas is produced by partially oxidising in a reactor vessel a gaseous fuel such as gaseous hydrocarbon, in particular petroleum gas or natural gas, at a temperature in the range of from 1000 °C to 1800 °C and at a pressure in
15 the range of from 0.1 MPa to 12 MPa abs. with the use of an oxygen-containing gas.

Synthesis gas will often be produced near or at a crude oil refinery because the produced synthesis gas can directly be applied as a feedstock for the
20 production of middle distillates, ammonia, hydrogen, methanol or as a fuel gas, for example, for heating the furnaces of the refinery or more efficiently for the firing of gas turbines to produce electricity and heat.

In gas burners applied in partial oxidation
25 processes for preparing synthesis gas it has appeared that the burner lifetime is restricted by phenomena of retraction of tips due to high temperature carburisation and oxidation. Because of such phenomena serious burner damage will occur and the on-stream time of the reactor
30 will be limited.

Therefore, there is a need for burners having a long lifetime which are less sensitive to the above phenomena than existing burners. A burner design has already been proposed wherein the overall flow and mixing pattern of
35 the reactants ensures that no burners parts come in

- 3 -

contact with hot gases from the combustion zone and this burner is capable of operating at high flame temperatures without burner-wear problems. (Vide the article "Improve syngas production using autothermal reforming" by T S Christensen and I I Primdahl in "Hydrocarbon Processing", March 1994, p. 42). However, if the flame is lifted from the burner this could lead to a product gas mixture of undesirable changing composition and to changing temperatures in the reactor. As a result, noise (level more than 120 dB) and strong mechanical vibrations of the burner and gasifier may occur. Such vibrations can be harmful to the refractory lining of the reactor.

It has now been found that the burner performance is influenced advantageously by flame stabilization and therefore care should be taken to stabilize the flame on the burner tips.

It is an object of the invention to provide a method for flame stabilization on the burner tips which solves the above problems.

The invention therefore provides a method for stabilizing the flame on the tips of burner internals in a process for preparing synthesis gas by partial oxidation of a gaseous hydrocarbon-containing fuel comprising the steps of:

- a) supplying a gaseous hydrocarbon-containing fuel, a moderator gas and an oxidiser through a burner to a reactor, wherein the mass flow of the moderator gas is adjusted such that the moderator gas concentration does not exceed a predetermined limit;
- b) effecting process conditions such that the flame is contacting the burner internal tips;
- c) re-adjusting the velocities and mass flows of the fuel and/or oxidiser and/or moderator gas in case of flame-lifting from the burner internal tips in such a

- 4 -

manner that the flame is restabilized on the burner internal tips; and wherein in step c) the moderator gas concentration does not exceed the said limit of step a).

5 An expert will know the general burner design conditions in which a flame contacts the burner tips.

10 In this manner the flame is stabilized on the burner internal tips and by applying a low amount of moderator gas it is possible to prepare a CO-rich product gas with a relatively high CO/H₂ ratio which is advantageous for downstream processes such as e.g. the Shell Middle Distillates Process (SMDS). The burner internal tips are made of a suitable material which is able to withstand such a flame, e.g. ceramic materials (e.g. silicon carbide or silicon nitride), noble metals or alloys thereof (e.g. Pt and/or Rh).

15 Since the flame at the burner exit generates a sound flame lifting from the burner internal tips can be observed by a change in noise level.

20 Noise levels are e.g. monitored by means of (piezo resistive) pressure transducers.

25 Another possibility to monitor flame lifting is optically e.g. by means of an optical probe which may be inserted into a burner channel, e.g. in the central channel of the burner. Flame lifting produces different flame spectra, which are analysed.

30 The invention is based upon the idea that in particular by means of adjusting the moderator gas concentration the flame position/stabilization with respect to the burner exit can be monitored at given process conditions such as throughput, pressure, temperature and the like. Flame monitoring/control is in particular of importance in case of natural gas feedstock changing in composition or recycle gas of varying composition being added to the natural gas feedstock.

35

- 5 -

Advantageously, moderator gas such as steam or CO₂ can be supplied e.g. with a velocity of 3-10 m/s in the channel between gaseous hydrocarbon-containing fuel and oxidiser. The channel width is e.g. 1-2 mm.

5 The invention will now be described by way of example in more detail by reference to Examples A, B and C.

Feed: Natural Gas with the following typical composition

| | | |
|----|----------------------------------|-------------------|
| | CH ₄ | : 94.4% by volume |
| 10 | C ₂ H ₆ | : 3.0% |
| | C ₃ H ₈ | : 0.5% |
| | C ₄ H ₁₀ | : 0.2% |
| | C ₅ H ₁₂ + | : 0.2% |
| | CO ₂ | : 0.2% |
| 15 | N ₂ | : 1.5% |

The supply temperature to the burner of this feedstock is 150-400 °C. The oxidiser is 99.5% pure O₂ with a supply temperature of 150-300 °C.

20 The burner is operating in the flame stabilised mode at a typical reactor pressure of 2-7 MPa and a reactor/syngas temperature of 1200-1500 °C. The moderator gas is steam.

25 Example A represents a burner wherein the fuel velocity is larger than the oxidiser velocity (fuel blast burner) and Examples B and C represent a burner wherein the oxidiser velocity is larger than the fuel velocity (oxygen blast burner).

| | A | B | C |
|---|------------------------------------|--|--|
| Number of passages: | 4 | 3 | 2 |
| Passage 1 feed velocity | oxidiser 20 to 50 m/s | fuel 20-50 m/s | oxidiser (blast flow) 80-120 m/s |
| Passage 2 feed velocity | fuel (blast flow) 50-100 m/s | oxidiser (blast flow) 80-120 m/s | fuel 20-50 m/s |
| Passage 3 feed velocity | oxidiser 20 to 50 m/s | fuel 20-50 m/s | - |
| Passage 4 feed velocity | fuel 20-50 m/s | - | - |
| Velocity ratio between the blast flow and the other flows | 2-4 | 2-4 | 2-4 |
| Steam in oxidiser | less than 30 vol% | less than 20 vol% | less than 20 vol% |

In the case that the natural gas feed also contains moderator gas, the maximum amount of moderator gas which can be added to the oxidiser need to be reduced to guarantee flame stabilization.

In the case that the moderator gas also contains CO₂ or N₂ the maximum molar concentration of moderator gas in the oxidiser may change to guarantee flame stabilization.

These reductions or changes are in accordance with the changes in the laminar flame velocity of premixed stoichiometric mixtures of the oxidiser and the fuel, such as is known by experts in the field.

- 7 -

In the case that the moderator gas is not added to the oxidiser until the burner exit but is injected via the small channel or slit between the oxidiser channel and the fuel channel, the moderator gas may also contain
5 CO, H₂ and hydrocarbons up to 20 vol% total. In this case the moderator gas flows through a slit of 1-2 mm wide at a typical velocity of 5-10 m/s.

It will be appreciated by those skilled in the art that any burner slit widths suitable for the purpose can
10 be applied, dependent on the burner capacity.

Advantageously, the first or central passage of the burner has a diameter up to 70 mm, whereas the remaining concentric passages have slit widths in the range of
1-20 mm.

15 It has appeared that when the oxidiser velocity is higher than the fuel velocity, the flame will lift from the burner internal tip, if the moderator gas concentration in the oxidiser is more than 20 vol%.

When the fuel velocity is higher than the oxidiser
20 velocity, it appears that the flame will lift from the burner internal tip if the moderator gas concentration in the oxidiser is more than 30 vol%.

Various modifications of the present invention will become apparent to those skilled in the art from the
25 foregoing description. Such modifications are intended to fall within the scope of the appended claims.

C L A I M S

1. A method for stabilizing the flame on the tips of burner internals in a process for preparing synthesis gas by partial oxidation of a gaseous hydrocarbon-containing fuel comprising the steps of:
 - 5 a) supplying a gaseous hydrocarbon-containing fuel, a moderator gas and an oxidiser through a burner to a reactor, wherein the mass flow of the moderator gas is adjusted such that the moderator gas concentration does not exceed a predetermined limit;
 - 10 b) effecting process conditions such that the flame is contacting the burner internal tips;
 - c) re-adjusting the velocities and mass flows of the fuel and/or oxidiser and/or moderator gas in case of flame-lifting from the burner internal tips in such a manner that the flame is restabilized on the burner internal tips; and wherein in step c) the moderator gas concentration does not exceed the said limit of step a).
2. The method as claimed in claim 1, wherein the burner is a multi-orifice (co-annular) burner comprising a concentric arrangement of n passages or channels coaxial with the longitudinal axis of said burner, wherein n is an integer ≥ 2 .
3. The method as claimed in claim 1 or 2, wherein the flame is monitored.
- 25 4. The method as claimed in claim 3, wherein the flame is monitored by noise detection, e.g. by means of pressure transducers.
5. The method as claimed in claim 3, wherein the flame is monitored optically.

- 9 -

6. The method as claimed in claim 5, wherein the flame is monitored by an optical probe inserted in a burner channel.

5 7. The method as claimed in claim 6, wherein the optical probe is inserted in the central channel of the burner.

8. The method as claimed in any one of claims 1-7, wherein the rims are made of ceramics, noble metals or alloys thereof.

10 9. The method as claimed in any one of claims 2-8, wherein the moderator gas is passed through a channel or slit between the gaseous hydrocarbon-containing fuel channel and the oxidiser channel.

15 10. The method as claimed in any one of claims 1-8, wherein the moderator gas is supplied with the gaseous hydrocarbon-containing fuel.

11. The method as claimed in any one of claims 1-8, wherein the moderator gas is supplied with the oxidiser.

20 12. The method as claimed in any one of claims 1-11, wherein the moderator gas is steam, water, carbon dioxide or a combination thereof.

25 13. The method as claimed in any one of claims 1-12, wherein the fuel velocity is higher than the oxidiser velocity and the mass flow of the moderator gas is adjusted such that the concentration of moderator gas in the oxidiser is less than 30 vol%.

30 14. The method as claimed in any one of claims 1-12, wherein the oxidiser velocity is higher than the fuel velocity and the mass flow of the moderator gas is adjusted such that the concentration of moderator gas in the oxidiser is less than 20 vol%.

INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/EP 96/02469

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B F23N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| P,A | US,A,5 458 808 (SUGGITT ROBERT M ET AL) 17 October 1995 see claim 1 --- | 1 |
| A | EP,A,0 082 634 (TEXACO DEVELOPMENT CORP) 29 June 1983 see claim 1 --- | 1 |
| A | US,A,4 836 831 (MARTENS FRANCISCUS J A) 6 June 1989 see claim 1 --- | 1 |
| A | EP,A,0 428 373 (CONTROL TECHTRONICS INC) 22 May 1991 see column 4, line 7 - column 5, line 19 ----- | 1 |

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 October 1996

Date of mailing of the international search report

29.10.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/02469

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US-A-5458808 | 17-10-95 | NONE | |
| EP-A-0082634 | 29-06-83 | US-A- 4390347 | 28-06-83 |
| | | US-A- 4390348 | 28-06-83 |
| | | US-A- 4474582 | 02-10-84 |
| | | CA-A- 1200103 | 04-02-86 |
| | | JP-A- 58125604 | 26-07-83 |
| | | US-A- 4474581 | 02-10-84 |
| US-A-4836831 | 06-06-89 | AU-B- 601276 | 06-09-90 |
| | | AU-A- 1589188 | 17-11-88 |
| | | CA-A- 1301458 | 26-05-92 |
| | | DE-A- 3869193 | 23-04-92 |
| | | EG-A- 18918 | 30-03-94 |
| | | EP-A- 0291111 | 17-11-88 |
| | | JP-A- 63297201 | 05-12-88 |
| | | NO-B- 174955 | 02-05-94 |
| | | SU-A- 1766282 | 30-09-92 |
| | | ZA-A- 8803292 | 14-11-88 |
| EP-A-0428373 | 22-05-91 | US-A- 5120214 | 09-06-92 |

THIS PAGE BLANK (USPTO)